Blends of Styrene-Butadiene-Styrene Triblock Copolymer with Random Styrene-Maleic Anhydride Copolymers

Piccini, Maria Teresa; Ruggeri, Giacomo; Passaglia, Elisa; Picchioni, Francesco; Aglietto, Mauro

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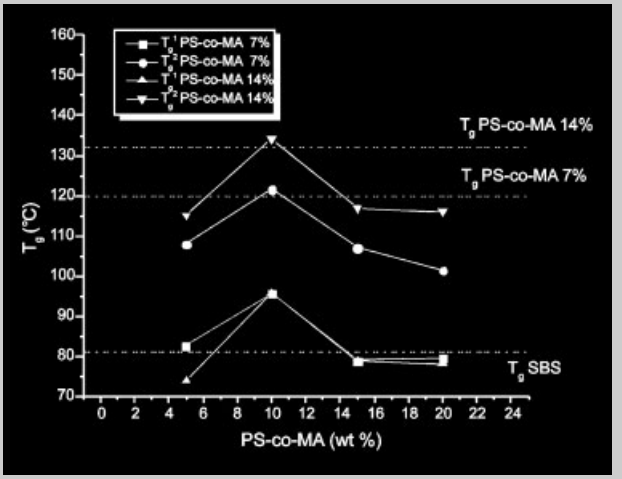
Full Paper: Blends of styrene-butadiene-styrene triblock copolymer (SBS) with random styrene-maleic anhydride copolymers (PS-*co*-MA), having different MA content, were prepared in a Brabender Plastigraph mixer. The presence of polystyrene (PS) blocks in the SBS copolymer and the high styrene content (93 and 86 wt.-%, respectively) in the two kinds of used PS-*co*-MA samples afforded a good compatibility between the PS phases of the two polymers. On the other hand, the presence of polar anhydride groups allows a net improvement of the thermal properties of the polystyrene phase of the blends as shown by differential scanning calorimetry (DSC) analysis. In addition, the dynamic behavior of the blends, as highlighted by dynamic thermo-mechanical analysis (DMTA), shows in all cases a ''stiffening'' of the material in comparison to original SBS. Preliminary experiments aimed to convert, directly in the mixer, the anhydride groups into the corresponding zinc salt allowed only a partial neutralization. Both DSC and scanning electron microscopy (SEM) indicate that the reaction is not complete under the used experimental conditions.



T_g against PS-*co*-MA content for SBS/PS-*co*-MA blends.

Blends of Styrene-Butadiene-Styrene Triblock Copolymer with Random Styrene-Maleic Anhydride Copolymers

Francesco Picchioni,[1] Elisa Passaglia,[2] Giacomo Ruggeri,[2] Maria Teresa Piccini,[2] Mauro Aglietto[2]*

[1] Department of Polymer Technology (SKT), Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands
E-mail: f.p.picchioni@tue.nl
[2] Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

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Introduction

The styrene-butadiene-styrene triblock copolymers (SBS) represent an interesting class of thermoplastic elastomers. In fact, these copolymers are characterized by a particular morphology which consists,[1–9] for typical PS contents of about 30 wt.-%, of a polybutadiene (PB) matrix in which polystyrene (PS) micro-domains, whose size is in the order of 10^2 nanometers, are dispersed. As a consequence, two different glass transition temperatures (T_g)[10] are observed: the first one, T_g(PB), at about $-100\,^{\circ}C$, corresponding to the PB phase, and the second one, T_g(PS), at about $+100\,^{\circ}C$ corresponding to the PS micro-domains. At temperatures between the two T_g's, the PB ''soft'' chains can freely move while the ''hard'' PS ones act as bridges between the rigid PS domains, i.e. they form a physically crosslinked network which remains stable at $T < T_g$(PS). Of course at $T > T_g$(PS) the PS chains are also free to move: this destroys the physical network, with consequent loose of properties, but allows also the material to be reprocessed for example after use.

During blending of SBS with PS,[11,12] the compatibility between PS and polystyrene domains of SBS is influenced by the relative molecular weights ratio $\overline{M}_n[h]/\overline{M}_n[c]$, where $\overline{M}_n[h]$ and $\overline{M}_n[c]$ are, respectively, the average molecular weight of the added PS homopolymer and of the PS blocks of the triblock copolymer. For values of $\overline{M}_n[h]/\overline{M}_n[c]$ less than 1 the added PS is soluble into the PS domains of SBS

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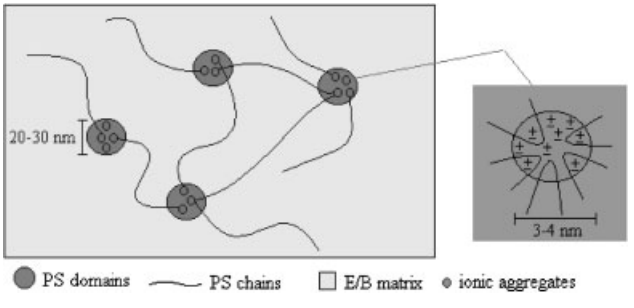
but very slight improvement of the thermal properties is observed. On the other hand, when $\overline{M}_n[h]/\overline{M}_n[c] \geq 1$, the solubility may be lower than in the previous case, but synergism in the thermal and dynamic behavior could clearly be observed, for example comparing the blends T_g with those of the pure components. In particular, these results were tentatively explained[11] on the basis of entanglement formation between the two components upon mixing, although no experimental confirmation of such hypothesis was presented. An even more pronounced improvement of the thermal behavior could be observed if polar groups were inserted into the PS domains of the triblock copolymer either by direct chemical modification[13–17] or by blending processes.[18] In particular, the sulfonation reaction of styrene-ethylene/1-butene-styrene (SEBS) triblock copolymer with consequent neutralization of the sulfonic acid moieties represents a convenient route to introduce ionic interactions in the PS ''hard'' phase.[13] The obtained morphology (Scheme 1) consists of ionomeric domains dispersed in the PS phase which shows a new transition,[14] due to the relaxation of the ionomeric domains, at $T > T_g$(PS). The overall result is anyway an improvement of the thermal and mechanical properties with respect to those of the neat triblock copolymer.

Random styrene-maleic anhydride copolymers (PS-*co*-MA), for which a detailed characterization of the random distribution of the MA comonomer was described only recently,[19,20] are attractive materials to be blended with SBS since, for low MA content, they could afford a good solubility into the SBS ''hard'' phase while carrying at the same time polar anhydride groups, which can be then converted into ionic species. Aim of this work was therefore to investigate the thermal and mechanical behaviors of the above-mentioned blends in particular as a function of the blends composition and MA content in the PS-*co*-MA copolymers. Furthermore, in order to introduce ionic interactions in the system, some preliminary experiments on the neutralization of the anhydride groups by zinc acetate $Zn(OAc)_2$ directly in dynamic conditions, i.e. during melt mixing with SBS, were performed.



Scheme 1. Schematic representation of sulfonated-SEBS morphology.

Experimental Part

Polymers

The block copolymer SBS (Calprene 501, Softer S.p.A, Forlì, Italy) was employed without further purification. It was characterized by a butadiene/styrene ratio of 69/31 (w/w), blocks average molecular weight 9 300-41 400-9 300 with $\overline{M}_w/\overline{M}_n = 1.5$ and vinyl units in the butadiene block of 10 wt.-% with respect to the total amount of butadiene units.

Two samples of PS-*co*-MA (Aldrich) were used without further purification. PS-*co*-MA 7% was characterized by the presence of 7 wt.-% maleic anhydride groups, melt index (230 °C, 16 kg, ASTM D 1238) of 1.7 g/10 min and $\overline{M}_w = 2.2 \times 10^5$. On the other hand, PS-*co*-MA 14 % was characterized by the presence of 14 wt.-% maleic anhydride groups, melt index (230 °C, 16 kg, ASTM D 1238) of 1.9 g/10 min and $\overline{M}_w = 2.0 \times 10^5$. Both copolymers were characterized before use by means of FT-IR analysis.

Zinc acetate dihydrate, $Zn(OAc)_2 \cdot 2H_2O$, from Rudipont, RGC grade, was used without further purification.

Characterization

FT-Infrared analysis: infrared spectra were performed by a Fourier Transform Spectrometer ''Perkin Elmer FT-IR 1750'' on films cast from a solvent solution on a KBr pellet.

Differential scanning calorimetry: DSC analyses were performed by a ''Perkin Elmer DSC7'' calorimeter equipped with a CCA7 cooling device. Mercury (m.p. −38.4 °C) and Indium (m.p. 156.2 °C) standards for low-temperature scans and Indium and Zinc (m.p. 419.5 °C) for high-temperature ones have been used for instrument calibration. Heating and cooling thermograms were carried out at standard rate of 20 °C/min.

Thermogravimetric analysis: all TGA thermograms were recorded by a Mettler TC11 instrument equipped with a Mettler M3 balance with an accuracy of 10^{-3} mg. Heating thermograms were carried out at a standard rate of 10 °C/min under dry nitrogen atmosphere.

Scanning electron microscopy analysis: all SEM micrographs were recorded on samples cryogenic fracture surfaces by a Jeol JSM mod.T-300 instrument at the Chemical Engineering Department of Pisa University.

Dynamic-mechanical thermograms (DMTA) were recorded by a Perkin-Elmer DMA7e instrument (three-point bending geometry). Thermograms were carried out at a standard heating rate of 1 °C/min and 1 Hz.

Preparation of Blends in the Brabender Mixer

The blends (SBS/PS-*co*-MA *x*% w/w, with $x = 7$, 14) were prepared in a Brabender Plastograph mixer under nitrogen atmosphere by introducing the desired amounts of the components in the mixer at 180 °C, rotor speed 50 rpm. After 10 min, the mixing was stopped and the materials recovered. The blends with zinc acetate, $Zn(OAc)_2$, were prepared according to the above-mentioned procedure; the calculated stoichiometric amount of the salt, with respect to the total amount of maleic anhydride groups, was added together with the polymers directly into the mixer.

Results and Discussion

Before blending SBS with PS-*co*-MA, attention was dedicated to the chemical characterization of PS-*co*-MA: in particular, the presence of carboxylic acid groups, which could be formed by hydrolysis, was investigated because of the possible influence on the miscibility.[18] The FT-IR analysis of the two PS-*co*-MA samples shows the presence of the characteristic absorptions at 1 780 cm^{-1} and 1 858 cm^{-1} due to symmetric and asymmetric stretching of anhydride group, and the absence of carboxylic acid characteristic absorptions demonstrating that no appreciable hydrolysis of anhydride groups has occurred.

Blends of SBS and PS-*co*-MA were prepared using an excess of SBS and, in particular, PS-*co*-MA concentrations of 5, 10, 15, and 20 wt.-% were used. All blends display (Table 1) two glass transitions temperatures at T over room temperature, thus indicating that two hard phases are formed upon melt mixing. The first transition (T_g^1) is close to that of SBS hard phase and can be assigned to a PS-rich phase with a low content of anhydride groups, while the second one (T_g^2) is quite similar to that of PS-*co*-MA so that it can be related to a PS-rich phase with high MA content. By plotting T_g values against blends composition (Figure 1) a maximum at 10 wt.-% PS-*co*-MA content is observed in all cases. This behavior held for the glass transition temperatures of the two hard phases and clearly indicates a synergism in the thermal properties for the 90/10 compositions since the T_g's for these blends are indeed even higher than those of the neat components. However, there seems to be no influence of the MA content in the PS-*co*-MA since maximums are always detected for 10 wt.-% of the random copolymer.

Table 1. DSC analysis (high temperatures) of SBS/PS-*co*-MA blends.

Run[a,b)]	T^1_g	T^2_g [c)]
	°C	°C
SBS	80.1	–
PS-*co*-MA 7%	–	120.0
PS-*co*-MA 14%	–	132.0
SBS/PS-*co*-MA 7% 95/5	82.7	108.1
SBS/PS-*co*-MA 7% 90/10	95.6	121.6
SBS/PS-*co*-MA 7% 85/15	79.0	107.1
SBS/PS-*co*-MA 7% 80/20	79.5	101.6
SBS/PS-*co*-MA 14% 95/5	73.8	115.1
SBS/PS-*co*-MA 14% 90/10	95.7	134.2
SBS/PS-*co*-MA 14% 85/15	78.9	117.0
SBS/PS-*co*-MA 14% 80/20	78.1	116.0
SBS/PS-*co*-MA 7% + $Zn(OAc)_2$ 90/10	88.7	n.d.
SBS/PS-*co*-MA 7% + $Zn(OAc)_2$ 80/20	79.6	101.7
SBS/PS-*co*-MA 14% + $Zn(OAc)_2$ 90/10	88.3	n.d.
SBS/PS-*co*-MA 14% + $Zn(OAc)_2$ 80/20	77.7	118.2

[a] Blends composition is expressed in weight ratios.
[b] Zinc acetate was used in stoichiometric amount with respect to the anhydride groups.
[c] Evaluated from 2nd-heat curves.

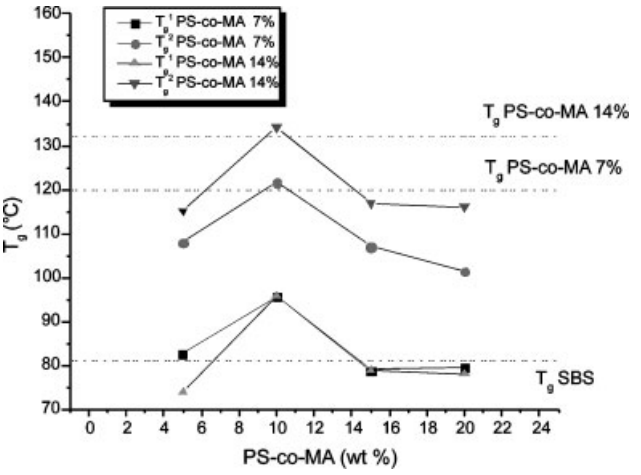
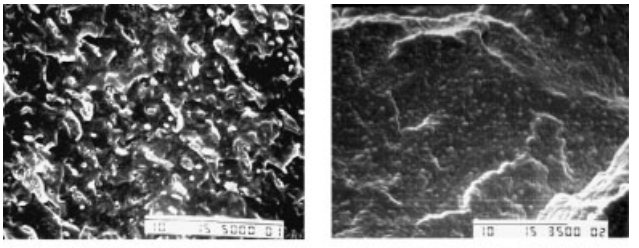


Figure 1. T_g against PS-*co*-MA content for SBS/PS-*co*-MA blends.

The morphology of the blends, as detected by SEM (some representative micrographs are reported in Figure 2), reveals the presence of at least two phases: a matrix in which white domains, which correspond[11] to the hard PS phases, are dispersed. However, the possibility of both microphase separation within the PS domains and of the macrophase segregation of PS-*co*-MA (especially for high PS-*co*-MA contents) cannot be excluded and may render the morphology much more complicated at more microscopic level. In any case, macrophase separation occurs not depending on blend composition and MA content in the copolymer, since all SEM micrographs are similar to each other.

Blends, characterized by means of TGA analysis (Table 2), show a degradation temperature (T_d) quite similar to that of neat SBS thus indicating that melt blending does not appreciably modify SBS thermal stability. Moreover, higher PS-*co*-MA content in the blends causes a decrease of T_d.

DMTA data (Table 3) outline the increase of the blends T_g, determined as onset in the storage modulus vs. tem-



SBS/PS-co-MA 7% 80/20 SBS/PS-co-MA 7% 90/10

Figure 2. SEM micrographs of SBS/PS-*co*-MA blends.

Table 2. TGA analysis of SBS/PS-*co*-MA blends.

Sample[a)]	T_d[b)]
	°C
SBS	430
PS-*co*-MA 7%	389
PS-*co*-MA 14%	375
SBS/PS-*co*-MA 7% 90/10	432
SBS/PS-*co*-MA 7% 80/20	402
SBS/PS-*co*-MA 14% 90/10	435
SBS/PS-*co*-MA 14% 80/20	419

[a)] Blends composition is expressed in weight ratios.
[b)] Evaluated as upturn point of TGA 1st-derivative curve.

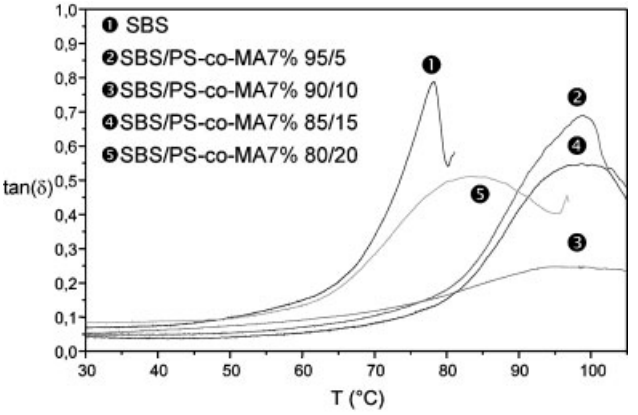


Figure 3. Tan(δ) curves for SBS/PS-*co*-MA 7% blends.

perature curves, with respect to that of neat SBS. The same observation can be extrapolated from the maximums of tan(δ) curves (Figure 3 and 4), which shift in general towards high temperature with respect to the virgin SBS. Moreover, blends with 5–10 wt.-% of PS-*co*-MA are characterized by the highest tan(δ) peak temperatures with respect to the other compositions. It must also be stressed that the evident broadening of tan(δ) peak corresponding to a 10 wt.-% PS-*co*-MA substantially agrees with what already has been reported in the literature[21] about similar systems and strongly addresses the synergism of properties for this particular composition. The relative decrease of the storage modulus in correspondence to the glass transition temperature of the blends hard phase displays its minimum values for the 90/10 compositions clearly indicating that these blends are much stiffer than the pure copolymer and the other mixtures. The fact that synergism takes place more evidently in correspondence of the 90/10 composition may suggest that in this case probably a saturation of the PS domains interface by the PS-*co*-MA component has already been achieved. Accordingly, for higher PS-*co*-MA contents, a new PS-rich phase could be formed by the excess PS-*co*-MA leading to phase separation and worsening of the mechanical properties. This hypothesis is in agreement to what already has been suggested in the literature[22] about SBS/PS blends, the only difference being in the fact that the solubility-limiting factor is not, in our case, the molecular weight of the added component but its amount with respect to the SBS triblock copolymer.

Some preliminary attempts to neutralize the MA groups in dynamic conditions, i.e. during processing, were performed by adding a stoichiometric amount of $Zn(OAc)_2$ directly into the mixer together with the two polymers. FT-IR spectra of the ''neutralized blends'' (Figure 5 and 6) show the presence of bands characteristic of the zinc-neutralized anhydride groups (at around 1 560 and 1 630 cm^{-1})[23,24] but also those of the unreacted MA groups, i.e. the neutralization reaction was not complete under the experimental conditions used. DSC analysis carried out on these blends (Table 1) shows a quite anomalous behavior. In fact, when using 10 wt.-% of PS-*co*-MA only one T_g was clearly detectable by DSC after

Table 3. DMTA analysis of SBS/PS-*co*-MA blends.

Sample[a)]	T_g	tan(δ)	$\Delta E/E$[b)]	ΔT[b)]
	°C	°C	%	°C
SBS	64.6	78.2	82.8	50–78
SBS/PS-*co*-MA 7% 95/5	86.8	98.9	87.9	50–100
SBS/PS-*co*-MA 7% 90/10	80.0	94.6	31.2	50–80
SBS/PS-*co*-MA 7% 85/15	78.2	93.8	n.d	–
SBS/PS-*co*-MA 7% 80/20	76.0	83.6	60.2	50–80
SBS/PS-*co*-MA 14% 95/5	87.7	98.5	53.2	50–80
SBS/PS-*co*-MA 14% 90/10	88.0	100.2	28.5	50–100
SBS/PS-*co*-MA 14% 85/15	76.2	97.5	28.4	50–80
SBS/PS-*co*-MA 14% 80/20	72.3	83.5	73.5	50–80

[a)] Blends composition is expressed in weight ratios.
[b)] Relative decrease of the storage modulus ($\Delta E/E$) calculated as $\frac{E^1(T_1)-E^1(T_2)}{E^1(T_1)} \cdot 100$ where the $T_1 - T_2 = \Delta T$ range has been chosen in order to comprise the hard phases glass transition temperature.

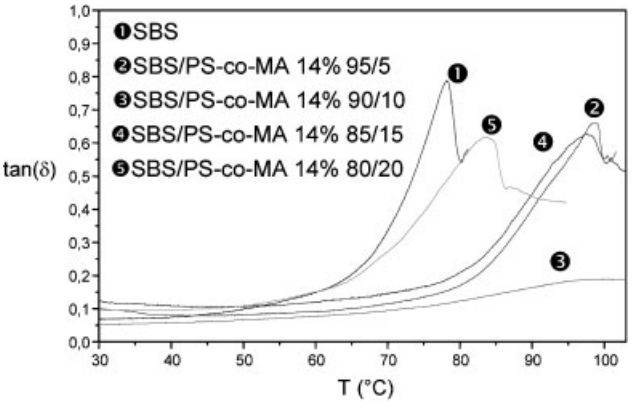


Figure 4. Tan(δ) curves for SBS/PS-*co*-MA 14% blends.

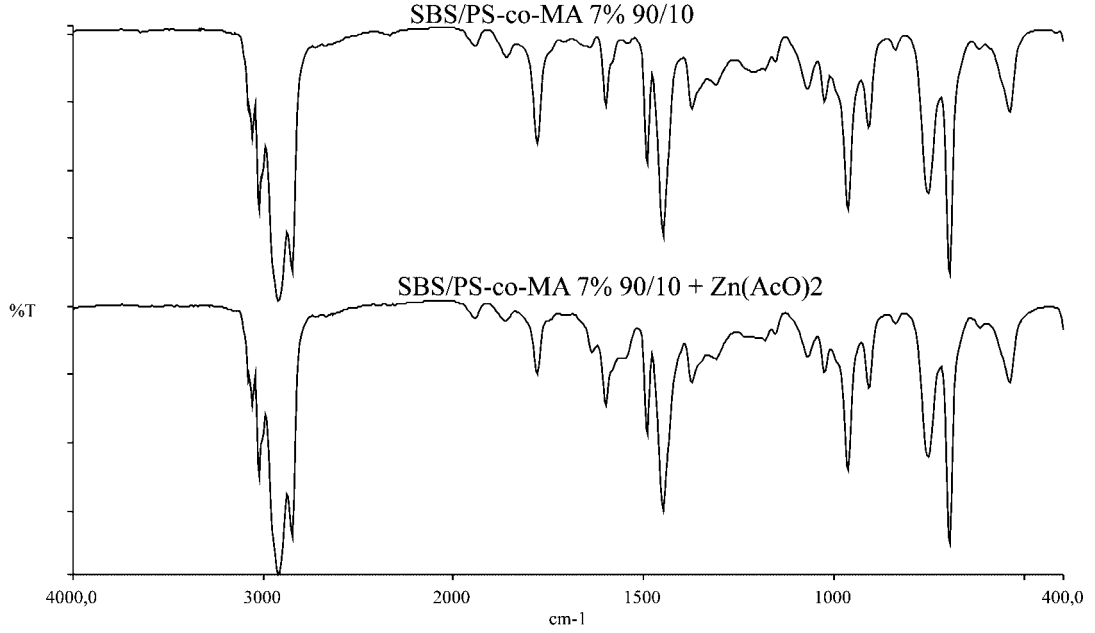


Figure 5. FT-IR spectra of SBS/PS-*co*-MA 7% 90/10 and SBS/PS-*co*-MA 7% 90/10 + $Zn(OAc)_2$.

neutralization, and its value is about 10 °C higher than the T_g of PS blocks in SBS. On the other hand, for blends with 20 wt.-% of PS-*co*-MA, two transitions are clearly detectable: the first one at about 80 °C is lower than T_g(PS), while the second one is in any case lower than the T_g of the corresponding PS-*co*-MA. It must be stressed that the broadening of the T_g in the presence of ionomeric species, as already reported in the literature,[13,14,21] creates substantial difficulties in the exact determination of the transition temperature and in general in the distinction within multiple transitions in a narrow temperature range. It is then possible only to outline, as a general trend, the fact that the neutralization of MA groups does not affect the blends thermal behavior in a positive way: comparison of thermal properties between blends with and without addition of zinc acetate clearly addresses a worsening of the thermal behavior in the former case. This evidence is also confirmed by DMTA data as depicted in Figure 7 for T_g values: for

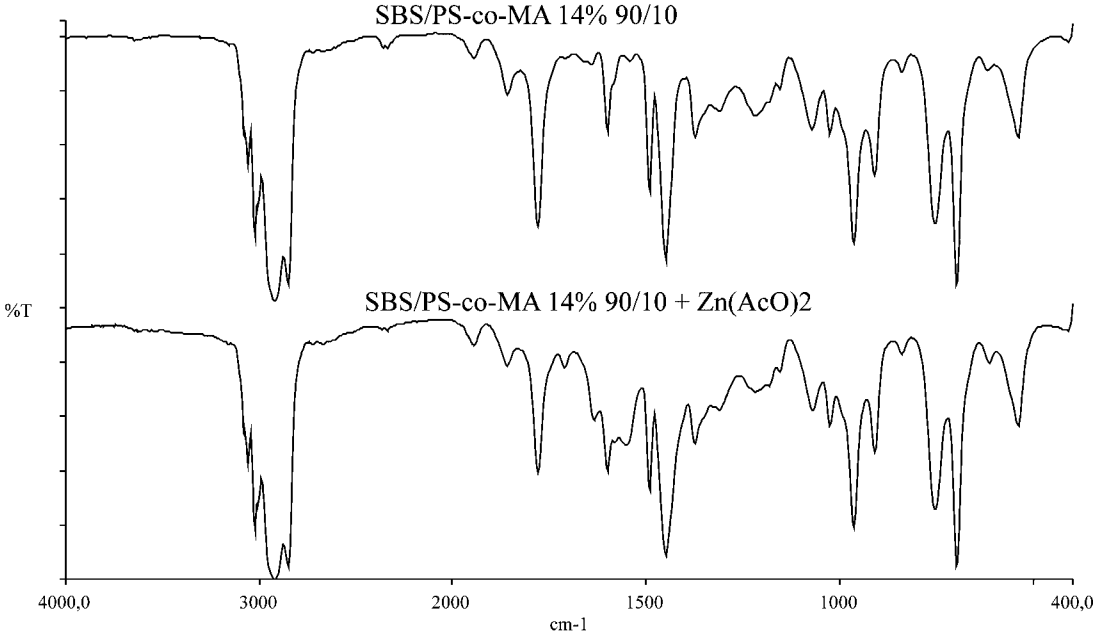


Figure 6. FT-IR spectra of SBS/PS-*co*-MA 14% 90/10 and SBS/PS-*co*-MA 14% 90/10 + $Zn(OAc)_2$.

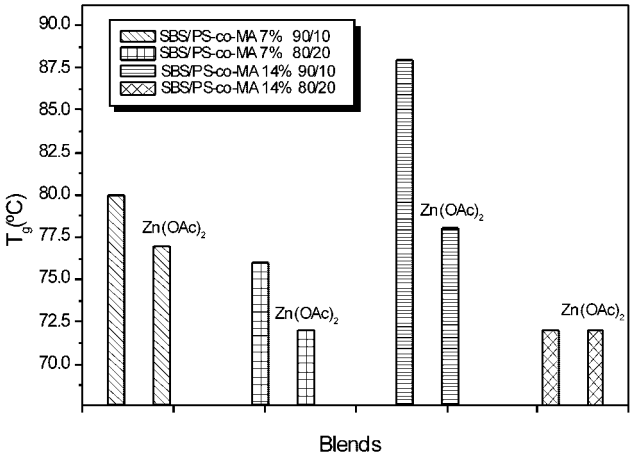


Figure 7. T_g, as determined by DMTA, for SBS/PS-*co*-MA by addition of $Zn(OAc)_2$.

any composition the addition of $Zn(OAc)_2$ results in no modification or in lower T_g values for the blends. These considerations suggest that an incomplete neutralization reaction can take place in the mixer resulting in the presence of unreacted $Zn(OAc)_2$ particles.

SEM micrographs (Figure 8a) show indeed the presence of white domains which correspond[18] to the hard PS phase of the blends containing both PS from SBS and PS-*co*-MA. However, microanalysis for zinc (8b) clearly demonstrates the presence of the latter mostly in the ''hard'' (white domains). Eventually (8c), when using the maximum amount of the salt (SBS/PS-*co*-MA 14%/$Zn(OAc)_2$ 80/20), it was even possible to detect the presence of unreacted zinc salt particles.

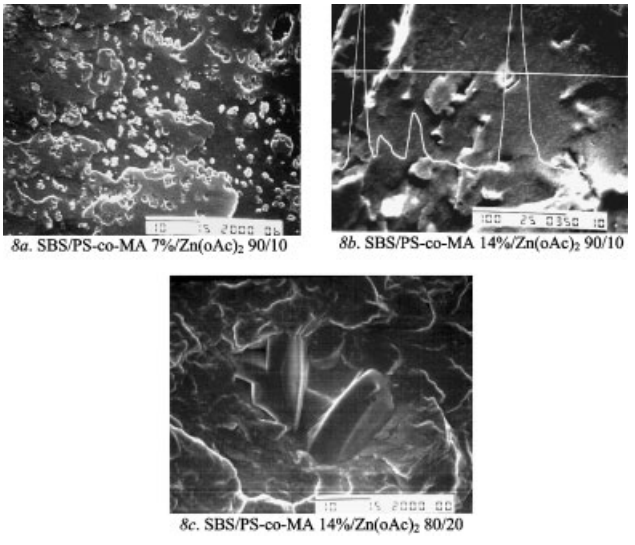


Figure 8. SEM micrographs of SBS/Ps-*co*-MA/$Zn(OAc)_2$ blends.

Conclusions

PS-*co*-MA copolymers blended in the melt with SBS triblock copolymer produced samples characterized by at least two hard phases. For the used PS-*co*-MA copolymers, the high $\overline{M}_n[h]/\overline{M}_n[c]$ values, where $\overline{M}_n[h]$ and $\overline{M}_n[c]$ are, respectively, the average molecular weight of the PS-*co*-MA component and that of the PS block of the triblock copolymer, resulted in the formation of two PS-based phases as clearly evidenced by DSC and SEM analysis. The first SBS hard phase can be assigned to a PS-rich phase with a low content of anhydride groups while the second one can be related to a PS-rich phase with high MA content.

However, even in these unfavorable conditions of solubility of PS-*co*-MA into the PS domains of SBS, a synergism in the mechanical and thermal properties was detected depending on the blends composition. This result is in agreement with what already has been reported in the literature for very similar systems and addresses anyway the ''stiffening'' of the SBS copolymer upon mixing as demonstrated by DMTA analysis.

Furthermore, the difference in the MA content seems to play only a minor role in determining the blends thermal and mechanical behavior. Synergistic effects take place almost for the same blends composition thus suggesting that the key parameter determining their occurrence is the $\overline{M}_n[h]/\overline{M}_n[c]$ ratio, which is nearly the same for the two used PS-*co*-MA samples.

Preliminary attempts for the neutralization of the anhydride groups directly while processing were unsatisfactory: worse thermal and mechanical properties were indeed observed with respect to the non-neutralized blends. The presence of unreacted salt particles is suggested by both DSC and SEM analysis and confirmed by the analysis of the FT-IR spectra, could account for the observed variations.

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